Inclusion of triphenylmethane derivatives by crown and linear O-containing molecules : selective interactions and crystal structures†

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The sulfamide derivative of triphenylmethanol, 3-[hydroxy(diphenyl)methyl]benzenesulfonamide ($H_2NSO_2Ph)Ph_2COH$ was synthesized and, alongside with the parent triphenylmethanol and triphenylmethylamine, was investigated for selective interactions with crown ethers of different dimensionality (12-18-membered cycles). The molecule of 12-crown-4 (12C4) appeared to be the best candidate for Ph_3COH, Ph_3CNH_2 and $Ph_3CNH_3 \cdot NCS$, while $(H_2NSO_2Ph)Ph_2COH$ forms the complex exclusively with 18-crown-6 (18C6). The triphenylammonia trifluoroacetate, $Ph_3CNH_3 \cdot CF_3COO$, selectively forms the complex only with 2-methoxyethanol. The crystalline products of the compositions $(Ph_3COH)_2 \cdot 12C4$, $(Ph_3CNH_2)_2 \cdot 12C4$, $(Ph_3CNH_3 \cdot NCS)_2 \cdot 12C4$, $[(H_2NSO_2Ph)Ph_2COH]_2 \cdot 18C6$ and $Ph_3CNH_3 \cdot CF_3COO\ CH_3OCH_2CH_2OH$ were obtained and studied by X-ray single crystal diffraction.

Introduction

Publication by Charles J. Pedersen of the synthesis of crown ethers and their property to form host–guest complexes with cations and comparatively small neutral guest molecules[1,2] has initiated the search and investigation of new, functionally isomorphous to crown ethers host molecules,[3–11] like cyclic cryptands, calixarenes and calixcrowns, cyclodextrines,[12] and acyclic molecules like aromatic diols,[8] arylureas,[13,14] derivatives of triphenylmethane (tritane)[7,9,14] *etc*. The numerous studies revealed the low selectivity of triphenylmethanol (tritanol, Ph_3COH) which binds in supramolecular complexes methanol, acetone, dimethyl formamide, dimethylsulfoxide, 1,4-dioxane, morpholine, piperidine, N-methylpiperazine, phenoxine,[9,15] tetrahydrofurane.[16] Triphenylsilanol Ph_3SiOH, the precise analogue of triphenylmethanol, in its turn forms stable adducts with dimethylsulfoxide and 1,4-dioxane due to O–H···O and C–H···π(arene) interactions.[17,18] Similarly, triphenylmethanaminium chloride forms an inclusion compound with acetone.[19] Now we are witnesses to the growing numbers of successful application of bulky host molecules. Thus, using excellent inclusion properties of bulky bisphenols Csöregh and co-workers[20] have stabilized carboxylic acid and ester molecules in a monomeric state for spectroscopic investigation. The recent research of Tohnai *et al.*[21] has demonstrated the triphenymethylamine ability for an efficient and robust fabrication of [4 + 4] ion-pair clusters consisting of a wide range of sulfonic acids with an emphasis on the efficiency of the combination of sterically hindered triphenylmethylamine and sulfonate ions (complementarity in hydrogen bonding, steric effects of the substituents, acidity of the sulfonic acids). In 1998 Hayashi *et al.*[22] showed on fluorosubstituted triphenylmethanol derivatives that the C–H···F(-C) interactions control the packing motif as well as the thermal stability of the crystal, in continuation in the hot *CrystEngComm* article Schollmeyer *et al.*[23] demonstrated that the trityl alcohols bearing three bromine or three iodine atoms at the *para*-positions of the aromatic units, as well as the fluorosubstituted derivatives of triphenylmethanol may be a very useful platform for analysing OH···π and halogen–π interactions as driving forces in crystal packing.

Surprisingly, apart from the two known examples of Ph_3SiOH[24] and Ph_3CSH[25] inclusion by 12-crown-4 (12C4), no systematic study of crown inclusion into the network of these bulky molecules has been carried out so far. This has motivated us to synthesize and study by X-ray diffraction the crystalline inclusion complexes of tritane derivatives with crown ethers of different dimensionality with an emphasis on the selectivity of interactions in these binary systems.

Experimental

Preparation of the crystalline inclusion compounds

It has been stated that spontaneous evaporation of solvents from the mixture of coronands **I–III** with triphenylmethanol (**IVa**), 1,1,1-triphenylmethanamine (**IVb**) and 1,1,1-triphenylmethanaminium thiocyanate (**IVc**) results in the crystalline molecular complexes of compositions $(\mathbf{IVa})_2.\mathbf{I}$ (complex **VI**), $(\mathbf{IVb})_2.\mathbf{I}$ (complex **VII**), $(\mathbf{IVc})_2.\mathbf{I}$ (complex **VIII**), respectively (Scheme 1).

The precipitation of **VI** from methanol solution indicates its higher stability in comparison with the triphenylmethanol complex with methanol.[9,15] The incorporation of the H-donor sulfamide group in the phenyl ring of **IVa** molecule yielding the

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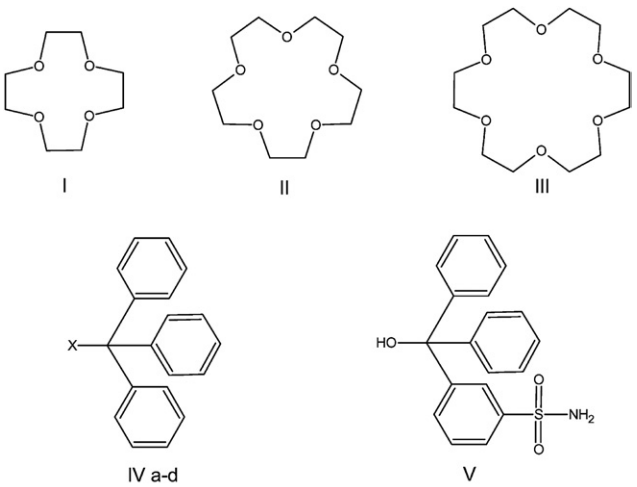

IV: X = OH (a), NH_2 (b), NH_3·SCN (c), NH_3·CF_3COO (d).

Scheme 1 Formulae of the substances used.

3-[hydroxy(diphenyl)methyl]benzenesulfonamide **V** drastically changes the mode of intermolecular recognition and results in the extraction of the largest 18C6 from the reaction mixture of **I, II, III** with the formation of the crystalline molecular complex of the composition (**V**)$_2$.**III** (complex **IX**). In previously reported studies no selectivity in the interaction of neutral molecules with the titled crown ethers was registered.[4] Moreover, the bulky di(benzenesulfonyl)amine $HN(SO_2C_6H_5)_2$ yields crystalline molecular complexes both with **I**[26] and **III**.[27–29] The replacement of the thiocyanate anion (**IVc**) by trifluoroacetate (**IVd**) dramatically changes the complexation process. From the methanolic mixture of **I, II, III**, compound **IVd** is reverted in an invariable form, while from the solution **IVd**–**I**–methanol–2-methoxyethanol the crystalline complex of triphenylmethanaminium trifluoroacetate with 2-methoxyethanol (compound **X**) is precipitated selectively. Thus, herein for the first time the selective interaction of bulky triphenylmethane derivatives with crown ethers is described with an emphasis on the possibility of crown ethers' separation[30] similar to the procedure described earlier.[31,32]

The initial chemicals were used as received from Aldrich without further purification. The ^{1}H NMR spectra were recorded with a Bruker AC 300 instrument at 300 MHz using tetramethylsilane as an internal reference. Thin-layer chromatography was conducted on Silufol plates with 1 : 8 methanol–chloroform as eluent and ninhydrin as developer. The crown ethers appeared as gray spots against a pink background.

Compound **V**, 3-[hydroxy(diphenyl)methyl]benzenesulfonamide: a mixture of 1,1′,1″-(chloromethanetriyl)tribenzene (2.788 g, 10 mmol) and chlorosulfonic acid (2.35 g, 20 mmol) was heated for 8 h at 150 °C and then cooled and poured onto 50 g of ice. The crystals were separated, placed into 40 ml of 25% aqueous ammonia, and heated with stirring for 12 h. The crystals that formed at 20 °C were washed with water, dried in air, and recrystallized from acetone–hexane (1 : 1). Yield: 1.80 g (53%), mp 188–190 °C, found, %: C 67.21; H 5.09; N 4.19; S 9.55, required for $C_{19}H_{17}NO_3S$: C 67.24; H 5.05; N 4.13; S 9.45. ^{1}H NMR ($CDCl_3$), *δ*, ppm: 7.27m, 7.44m (14H, CH).

Compound **VI**, triphenylmethanol–1,4,7,10-tetraoxacyclododecane, 2 : 1 : triphenylmethanol (260 mg, 1 mmol) and a mixture of 1,4,7,10-tetraoxacyclododecane (176 mg, 1 mmol), 1,4,7,10,13-pentaoxacyclopentadecane (220 mg, 1 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (264 mg, 1 mmol) were dissolved in methanol (10 ml) The colorless, transparent crystals were obtained by slow evaporation of solvents at room temperature for several days. Yield: 593 mg (85%), mp 147–148 °C, found, %: C 79.28; H 6.94, required for $C_{46}H_{48}O_6$: C 79.33; H 6.90. ^{1}H NMR ($CDCl_3$), δ, ppm: 1.62 (s 2H, OH), 3.70 (s, 16H, CH_2), 7.24–7.35 (m, 30H, CH).

Compound **VII**, 1,1,1-triphenylmethanamine–1,4,7,10-tetraoxacyclododecane, 2 : 1 : 1,1,1-triphenylmethanamine (259 mg, 1 mmol) and a mixture of 1,4,7,10-tetraoxacyclododecane (176 mg, 1 mmol), 1,4,7,10,13-pentaoxacyclopentadecane (220 mg, 1 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (264 mg, 1 mmol) were dissolved in a mixture of benzene/diethyl ether (1 : 2, 5 ml). The colorless, transparent crystals were obtained by slow evaporation of solvents at room temperature for several days. Yield: 495 mg (71%), mp 94–95 °C, found, %: C 79.51; H 7.25; N 4.03, required for $C_{46}H_{50}N_2O_4$: C 79.53; H 7.24; N 4.05. ^{1}H NMR ($CDCl_3$), δ, ppm: 1.86 (s, 4H, NH), 3.70 (s, 16H, CH_2), 7.20–7.32 (m, 30H, CH).

Compound **VIII**, triphenylmethanaminium thiocyanate–1,4,7,10-tetraoxacyclododecane, 2 : 1 : triphenylmethanaminium thiocyanate (318 mg, 1 mmol) and a mixture of 1,4,7,10-tetraoxacyclododecane (176 mg, 1 mmol), 1,4,7,10,13-pentaoxacyclopentadecane (220 mg, 1 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (264 mg, 1 mmol) were dissolved in methanol (15 ml). The colorless, transparent crystals were obtained by slow evaporation of solvents at room temperature for several days. Yield: 650 mg (80%), mp 170–172 °C, found, %: C 70.85; H 6.48; N 6.93; S 7.89, required for $C_{48}H_{52}N_4O_4S_2$: C 70.90; H 6.45; N 6.89; S 7.93. ^{1}H NMR ($CDCl_3$), δ, ppm: 3.70 (s, 16H, CH_2), 7.09–7.45 (m, 30H, CH).

Compound **IX**, 3-[hydroxy(diphenyl)methyl]benzenesulfonamide–1,4,7,10,13,16-hexaoxacyclooctadecane, 2 : 1 : 3-[hydroxy(diphenyl)methyl]benzenesulfonamide (340 mg, 1 mmol) and a mixture of 1,4,7,10-tetraoxacyclododecane (176 mg, 1 mmol), 1,4,7,10,13-pentaoxacyclopentadecane (220 mg, 1 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (264 mg, 1 mmol) were dissolved in a mixture of acetone/hexane (1 : 1, 15 ml). The colorless, transparent crystals were obtained by slow evaporation of solvents at room temperature for several days. Yield: 835 mg (98%), mp 174–176 °C, found, %: C 63.71; H 6.24; N 2.99; S 6.85, required for $C_{50}H_{58}N_2O_{12}S_2$: %: C 63.67; H 6.20; N 2.97; S 6.85. ^{1}H NMR (CD_3OD), δ, ppm: 3.62 (s, 24H, CH_2), 7.27–7.44 (m, 28H, CH).

Compound **X**, triphenylmethanaminium trifluoroacetate–2-methoxyethanol, 1 : 1 : triphenylmethanaminium trifluoroacetate (373 mg, 1 mmol) (373 mg, 1 mmol)) and 1,4,7,10-tetraoxacyclododecane (176 mg, 1 mmol) were dissolved in a mixture of methanol/2-methoxyethanol (1 : 1, 10 ml). The colorless, transparent crystals were obtained by slow evaporation of solvents at room temperature for several days. Yield: 380 mg (85%), mp 155–156 °C, found, %: C 64.13; H 5.80; N 3.19; F 12.64, required for $C_{24}H_{26}F_3NO_4$: %: C 64.18; H 5.83; N 3.12; F 12.68. ^{1}H NMR (DMSO), δ, ppm: 2.49 (s, 3H, CH_3), 3.49 (s, 4H, CH_2), 7.05–7.44 (m, 30H, CH).

Crystallographic studies

The X-ray intensity data for **VI–X** were recorded at room temperature on a Bruker SMART 1000 CCD area detector diffractometer employing graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) in ϕ and ω scan mode. Final unit cell dimensions and positional data were obtained and refined on an entire data set. Integration and scaling resulted in a data set corrected for Lorentz and polarization effects using DENZO.[33] The scaling as well as global refinement of the crystal parameters were performed by SCALEPACK.[33] The absorption correction for **VI**, **VIII**, **IX** was applied using SADABS.[34] The structure solution and refinement proceeded similarly using SHELX-97 program package[35] for all structures. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. Some disorder was found in **IX** and **X**: in **IX** the O6 and C24 atoms of the macrocyclic ring are disordered over two positions with partial occupancies of 0.90(1) and 0.10(1), and only the major component was refined in an anisotropic approximation. In **X** the triflate anion, CF_3COO^- and 2-methoxyethanol molecule were modeled in such a way that anionic F and O atoms and CH_3–O–CH_2–CH_2– fragment of the 2-methoxyethanol molecule were disordered over two positions with partial occupancies of 0.58(1) and 0.42(1), respectively; both positions were refined in an anisotropic approximation. In all structures C–bound H atoms were placed in calculated positions and were treated using a riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$. The O- and N-bound H-atoms were determined from a difference Fourier map and were then allowed to refine isotropically with $U_{iso}(H) = 1.5U_{eq}(O,N)$. DFIX restraints were applied to the N–H distances ($d = 0.86$ Å) in **VII** and **VIII**. Crystal data together with further details of data collections and refinement calculations are given in Table 1. CCDC reference numbers 690773–690777.

Results and discussion

Crystallographic description of the complexes

Compounds **VI** and **VII** crystallize in the same triclinic space group *P*1 and have close unit cell dimensions, as is evident from Table 1. For both compounds the asymmetric unit comprises one half of the 12C4 molecule that resides on an inversion center and one Ph_3COH or Ph_3CNH_2 molecule in general position (Fig. 1). The geometry of the Ph_3COH (Ph_3CNH_2) and 12C4 molecules is in agreement with the literature data.[24,25,36–38] The components are associated in the 1 : 2 molecular complexes *via* two single OH···O (NH···O) hydrogen bonds (Table 2).

The crystal packing in **VI** and **VII** is dictated by the combination of conventional OH···O (NH···O) hydrogen bonds that combine the molecules in the 1 : 2 complex, weak CH(arene)··· O(crown) interactions that combine the complexes in the tape with the hydrophobic exterior formed by the phenyl rings (Fig. 2), and the concerted sextuple phenyl embrace (SPE)[39] between the Ph_3COH (Ph_3CNH_2) molecules in the neighboring tapes. Four host molecules surround each 12C4 molecule in the tape. The packing in **VII** is characterized by slightly increased distances analogous to those shown in Fig. 2a for **VI** with the second hydrogen of the amino group being free of any involvement in hydrogen bonding (very similar to the pure phase of Ph_3CNH_2).[37]

This ordering function of 12C4 molecule in **VI** and **VII** is looking very amazing in confrontation with the relative although rather restrictive examples available in CSD:[40] thus, inclusion of a dioxane molecule in the network of isostructural Ph_3COH[36] or Ph_3SiOH[17] molecules results in the 1 : 1 adduct in the first case and 1 : 2 adduct in the second one with pronounced changes in the crystal packing, although both compounds crystallize in the same triclinic crystal system. On the other hand, the same hosts yield the isostructural 2 : 1 aggregates with dimethylsulfoxide, both being crystallized in the same *C*2/*c* space group with close

Table 1 Summary of the crystal data of the five studied compounds, **VI–X**, and structure refinement parameters

Compound	VI	VII	VIII	IX	X
Composition	$2C_{19}H_{16}O{\cdot}C_8H_{16}O_4$	$2C_{19}H_{17}N\ C_8H_{16}O_4$	$2(C_{19}H_{18}N{\cdot}NCS){\cdot}C_8H_{16}O_4$	$2C_{19}H_{17}NO_3S{\cdot}C_{12}H_{24}O_6$	$C_{19}H_{18}N{\cdot}C_2F_3O_2\ C_3H_8O_2$
CCDC number	690773	690777	690776	690775	690774
Formula weight	696.84	694.88	813.06	943.10	449.46
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*1	*P*1	$P2_1/c$	*P*1	*C*2/*c*
a /Å	8.3614(7)	8.4675(8)	14.7301(15)	8.4707(6)	17.069(4)
b /Å	10.4963(9)	10.2973(13)	16.1984(16)	12.4699(9)	10.694(3)
c /Å	11.710(1)	11.943(2)	9.729(1)	12.8600(9)	26.520(7)
α/°	82.114(2)	84.058(9)	90.0	115.372(1)	90.0
β/°	86.716(2)	88.008(12)	103.97(2)	97.929(1)	107.367(5)
γ/°	66.740(2)	67.966(8)	90.0	99.540(1)	90.0
V /Å^3	935.25(14)	960.1(2)	2252.7(4)	1176.63(14)	4620(2)
Z	1	1	2	1	8
D_c /Mg m^{-3}	1.237	1.202	1.199	1.331	1.292
μ(MoKα)/mm^{-1}	0.081	0.076	0.165	0.179	0.103
F(000)	372	372	864	500	1888
Reflections collected / unique	5310/ 3605 [R(int) = 0.020]	3625 / 3373 [R(int) = 0.026]	12820 / 4413 [R(int) = 0.043]	6829 / 4541 [R(int) = 0.015]	12877 / 4554 [R(int) = 0.024]
Reflections with $I>2\sigma(I)$	2978	2622	1462	3154	3066
Goodness-of-fit	1.060	1.042	0.831	0.925	1.011
R, wR [$I>2\sigma(I)$]	0.048, 0.138	0.041, 0.111	0.054, 0.117	0.039, 0.096	0.043, 0.121

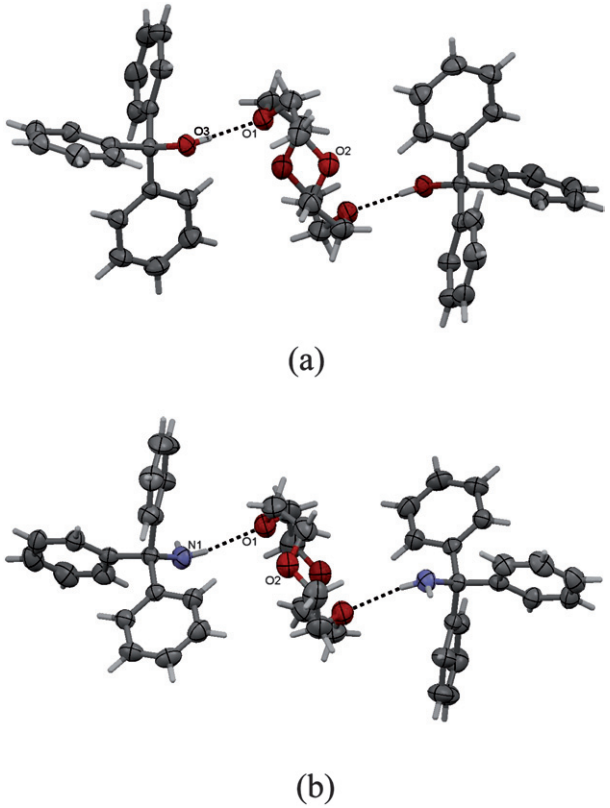

Fig. 1 ORTEP drawing (a) for **VI**, (b) for **VII** with a partial numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

unit cell dimensions.[15,17] Ferguson and co-workers[36] analysing the series of the group 14 Ph_3MOH molecules (M = C, Si, Ge, Sn, Pb) revealed for them different crystal packing motifs: the C-, Si- and Ge-[17,41] derivatives represent hydrogen-bonded tetramers with the O-atoms in a flatten tetrahedral arrangement, while Sn- and Pb-containing molecules have structures consisting of zigzag chains of planar Ph_3M (M = Sn, Pb) groups joined by OH groups giving trigonal bipyramidal geometry at M,[42] whilst in Ph_3CSH,[43] a precise analogue of Ph_3COH as well as in $PhCNH_2$,[37] being isoelectronic with Ph_3COH, there are no intermolecular hydrogen bonding despite the availability of potential H-donors (SH, NH_2 groups) and H-acceptors (S, N-lone pair), and the structures consist of isolated molecules with no indication that the H-atoms take part in any hydrogen bonding. Concluding this section, the row of the relative crown-containing binary systems $(Ph_3COH)_2.12C4$ (**VI**), $(Ph_3CNH_2)_2.12C4$ (**VII**) (present work), $(Ph_3SiOH)_2.12C4$,[24] and $(Ph_3CSH)_2.12C4$[25] represents the isomorphous aggregates with close unit cell dimensions and a common structural motif. It permits to conclude the ordering and leveling function of the 12C4 molecule upon its inclusion.

The view of complex **VIII** is shown in Fig. 3. The ternary salt-like adduct **VIII** crystallizes in the centrosymmetric space group $P2_1/c$ and, similar to **VI** and **VII**, the 12C4 molecule resides on an inversion center. The components in the crystal are held together *via* the diverse system of charge-assisted hydrogen bonds, $NH^+\cdots O$(crown), $NH^+\cdots N^-(NCS^-)$ and $NH^+\cdots S^-(NCS^-)$ (Fig. 3, Table 2).

The tetrahedral ammonia group provides one hydrogen for the $NH^+\cdots O$ interaction with a crown molecule and two hydrogens for interionic $NH^+\cdots N^-(NCS^-)$ and $NH^+\cdots S(NCS^-)$ interactions with two inversion-related NCS^- anions. Just as in the two

Table 2 Hydrogen bond distances (Å) and angles (°) for **VI–X**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)	Symmetry transformation for acceptor
VI					
O(3)–H(3A)···O(1)	0.89(2)	1.94(2)	2.814(2)	169(2)	*x, y, z*
C(19)-H(19A)···O(2)	0.93	2.61	3.380(2)	141	*x, y, z*
C(8)-H(8A)···O(2)	0.93	2.59	3.482(2)	162	*x, y − 1, z*
VII					
N(1)–H(1N)···O(1)	0.89(2)	2.22(2)	3.087(2)	168(2)	*x, y, z*
C(19)-H(19A)···O(2)	0.93	2.66	3.426(2)	140	*x, y, z*
C(8)-H(8A)···O(2)	0.93	2.65	3.493(2)	152	*x, y − 1, z*
VIII					
N(1)–H(2N)···O(1)	0.89(2)	1.92(2)	2.790(3)	166(3)	*x, y, z*
N(1)–H(3N)···N(2)	0.90(2)	2.01(2)	2.892(4)	166(3)	*x, y, z*
N(1)–H(1N)···S(1)	0.90(2)	2.35(2)	3.246(3)	170(3)	*−x + 1, −y + 2, −z + 1*
IX					
O(3)–H(1O)···O(2)	0.77(2)	2.16(2)	2.917(2)	169(2)	*−x, −y, −z*
N(1)–H(1N)···O(5)	0.82(2)	2.37(2)	3.029(2)	138(2)	*x, y − 1, z*
N(1)–H(1N)···O(6)	0.82(2)	2.51(2)	3.086(2)	129(2)	*x, y − 1, z*
N(1)–H(2N)···O(4)	0.88(2)	2.25(2)	3.013(2)	145(2)	*−x, −y, −z*
N(1)–H(2N)···O(5)	0.88(2)	2.41(2)	3.135(2)	140(2)	*−x, −y, −z*
X					
N1–H(2N)···O(1)	0.94(2)	1.95(2)	2.877(5)	174(2)	*x, y, z*
N1–H(2N)···O(1′)	0.94(2)	1.98(2)	2.886(6)	162(2)	*x, y, z*
N1–H(1N)···O(2)	0.93(2)	1.93(2)	2.862(2)	177(2)	*−x, y, −z + 1/2*
N1–H(3N)···O(3)	0.95(2)	1.80(2)	2.752(11)	179(2)	*x, y, z*
N1–H(3N)···O(3′)	0.95(2)	1.82(2)	2.766(14)	174(2)	*x, y, z*
O(2)–H(2B)···O(4)	0.95(2)	1.71(3)	2.658(10)	173(2)	*x, y, z*
O(2)–H(2B)···O(4′)	0.95(2)	1.69(3)	2.640(10)	171(2)	*x, y, z*

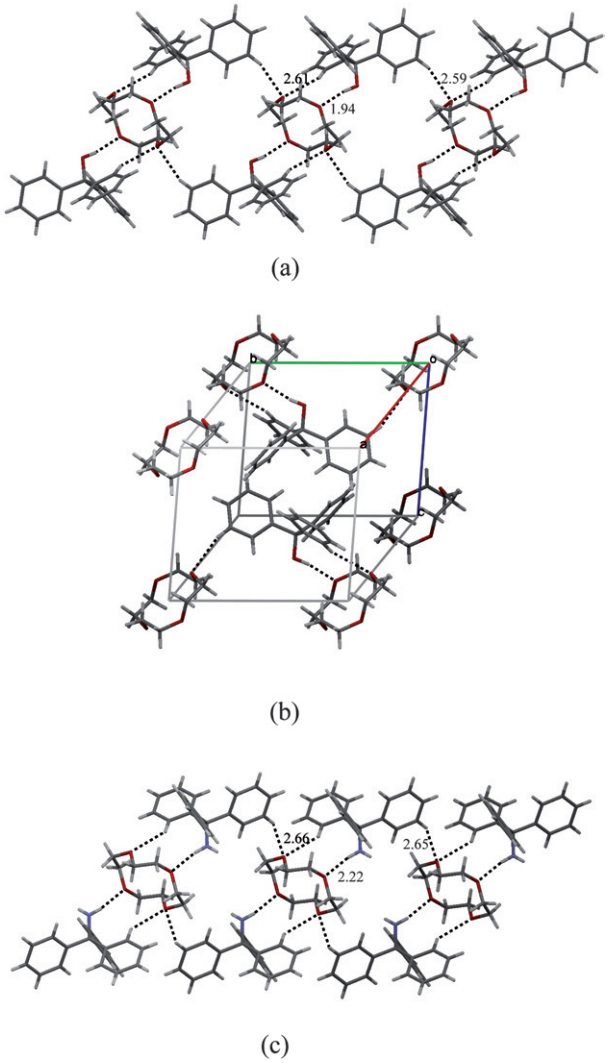

Fig. 2 Crystal packing for **VI** and **VII**, (a) fragment of tape in **VI** with the shortest C–H···O distances shown by dashed lines, (b) fragments of adjacent tapes with SPE between two Ph_3COH molecules, (c) fragment of tape in **VII** with the shortest N–H···O and C–H···O distances shown by dashed lines.

previous structures, these concerted interactions combine the components in the tape propagated along the *c* axis in the crystal (Fig. 4). The neighboring tapes are packed in an antiparallel

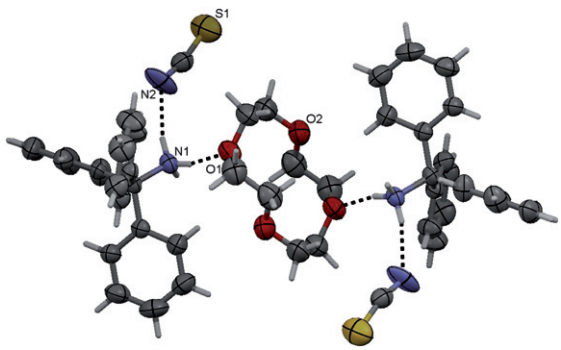

Fig. 3 ORTEP drawing for **VIII** with a partial numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

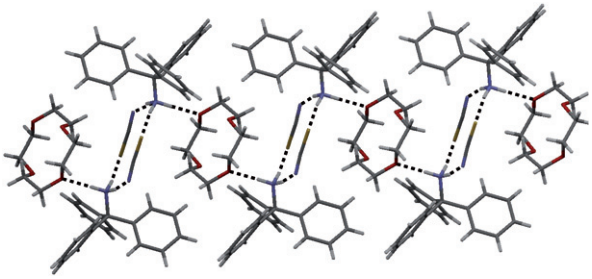

Fig. 4 Fragment of tape in **VIII**.

arrangement to maximize the SPE. The crystal architecture of **VIII** is very close to structure organization in tritylammonium chloride 1,4-dioxane solvate, $Ph_3CNH_3Cl.(CH_2CH_2O)_2$ (YAGSIJ refcode in CSD).[44]

As was stressed above, incorporation of the amidosulfoxide group into the phenyl ring of **IVa** results in competition between the two donor groups (SO_2NH_2 and OH) of **V** for the crown's oxygens and following the Etter's rule[45] in a preferable interaction of the stronger H-donor, SO_2NH_2 group with the macrocyclic oxygens *via* two bifurcated NH···O hydrogen bonds with the formation of 1 : 2 molecular complex **IX** (Fig. 5, Table 2). **IX** crystallizes in triclinic space group *P*1 where the 18C6 molecule resides on an inversion center. The hydroxyl group seeking for the next H-acceptor is responsible for the association of these complexes into tapes *via* OH···O(SO_2) hydrogen bonds (Fig. 6, Table 2). Similar to the previous examples, the tape in **IX** is characterized by the hydrophilic interior saturated by hydrogen bonds and two external hydrophobic sides formed by the phenyl rings. Compound **IX** represents the first known example of the inclusion of spacious 18C6 molecule in the lattice of triphenylmethanol derivative. The common feature of the crystal packing for **VI**–**IX** is a ribbon motif with crown inclusion within the ribbon and the SPE formulated between the neighboring ribbons.

Compound **X** of the 1 : 1 : 1 stoichiometry is formed as a result of the interaction of **IVd** with a linear 2-methoxyetanol molecule. **X** crystallizes in monoclinic space group *C*2/*c*. The content of the asymmetric unit is shown in Fig. 7. Similar to **VIII** it is a ternary complex where two hydrogens of the same ammonia group are involved in the NH^+···O(COO^-) and NH^+···O(2-methoxyethanol) contacts (Table 2). Furthermore, inside the complex the terminal hydroxyl group of the 2-methoxyethanol molecule participates in OH···O^-(COO^-) interaction with the second carboxyl oxygen. These three hydrogen bonds close the eleven-membered ring, $R_3^3(11)$ using a graph set notation.[45]

Contrary to **VIII** where each ammonia group interacts with two anions and one neutral crown molecule, in **X** the third ammonia hydrogen is involved into NH^+···O interaction with the second 2-methoxyethanol molecule related by the two-fold axis with the basic one. These concerted interactions combine two complexes into a six-membered calix-like capsule stabilized by 8 charge-assisted hydrogen bonds within the hydrophilic core that is covered by the hydrophobic exterior formed by six phenyl rings of two tritylammonia cations and two terminal methyl groups of 2-methoxyethanol molecules (Fig. 8). The CH···F interactions[22,23,46] between triflate anion and 2-methoxyethanol

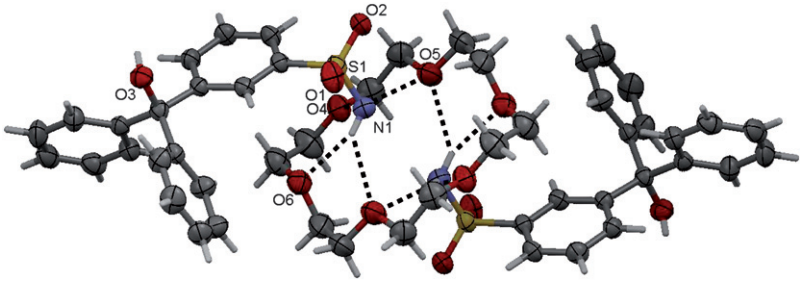

Fig. 5 ORTEP drawing for **IX** with a partial numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

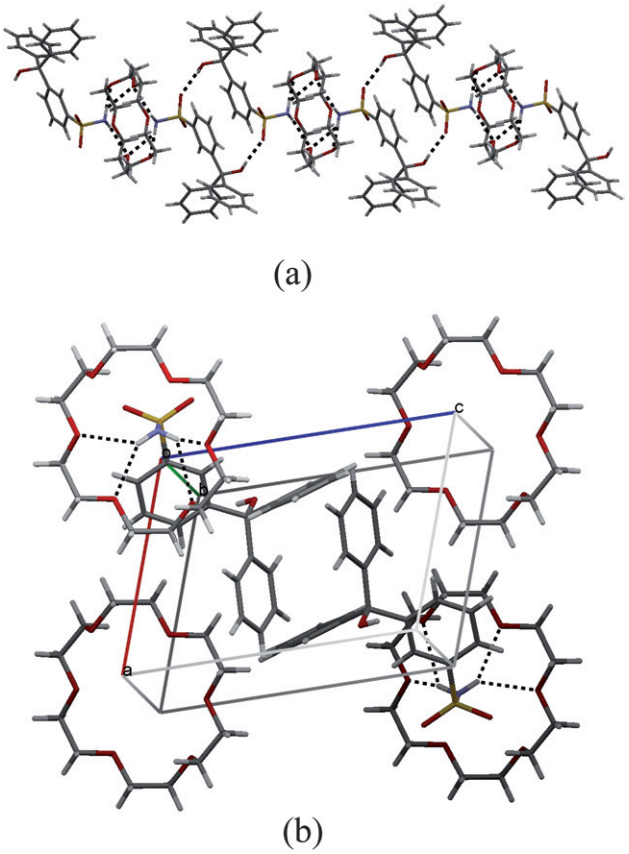

Fig. 6 Packing diagram for **IX** (a), fragment of tape (b), fragments of adjacent tapes with SPE between two **V** molecules.

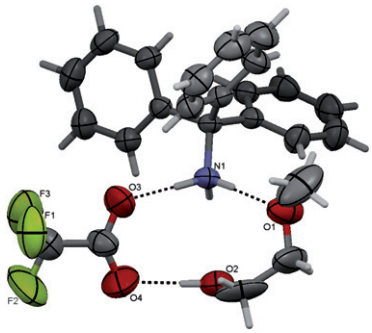

Fig. 7 ORTEP drawing for **X** with the partial numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

molecule are responsible for the association of the 6-membered globules into tape running along the *b* direction in the crystal.

Thus, the present study amplifies the scanty family of trytilammonia salts by two novel representatives. Contrary to the trytile sulfonates studied so far[21] all of which represent binary adducts and formulate the well-defined [4 + 4] ion-pair clusters, **VIII** and **X** alongside the tritylammonium chloride acetone and tritylammonium chloride dioxane solvates [19,44] belong to the ternary compounds with the inclusion of the different O-containing neutral molecules (acetone, dioxane, 12C4, 2-methoxyethanol) in the ionic crystal lattice of the parent salt. The size and topology of these guests appear to be crucial for the final aggregates: linear acetone and 2-methoxyethanol molecules facilitate the formation of the isolated 6-membered clusters while the cyclic double-face 1,4-dioxane and 12C4 molecules provide extended 1D structures. In any closest environment [three anions,[21] two anions and one neutral molecule[19,44] or one anion and two neutral molecules (present work)] all three ammonium hydrogens are involved in the hydrogen bonding system.

Conclusions

For the first time the approaches of supramolecular chemistry were used to estimate the preferable in size crown ethers (in the order of 12–18-membered CEs) for interaction with triphenylmethane derivatives. The 12C4 molecule has proven to be the best candidate as it is selectively included in the crystal lattice of neutral Ph_3COH and Ph_3CNH_2 in the 1 : 2 ratio and in the ionic network of Ph_3CNH_3NCS in the 1 : 1 : 1 ratio. Contrary to the pure forms of Ph_3COH, Ph_3SiOH, Ph_3CSH, and Ph_3CNH_2 which differ essentially by the crystal packing, the corresponding binary aggregates with 12C4 appear to be isomorphous and ordered with each macrocyclic molecule entrapping by four bulky host molecules. The functionalization of one of the phenyl rings in the Ph_3COH molecule by the H_2NSO_2-group provides its involvement in the interaction with 18C6 in a traditional manner and excludes the hydroxyl group from the host–guest interactions. The supramolecular architecture of the studied tritylammonium salts is dictated by the concerted effect of the topology of the anion and the included neutral molecule, being 1D structure for $Ph_3CNH_3 \cdot NCS$ assimilating cyclic 12C4 molecule and the isolated six-membered capsule upon inclusion of linear 2-methoxyethanol molecules in the ionic lattice of $Ph_3NH_3 \cdot CF_3COO$. In all cases the common packing motif maximizes the SPE arrangement of the host molecules.

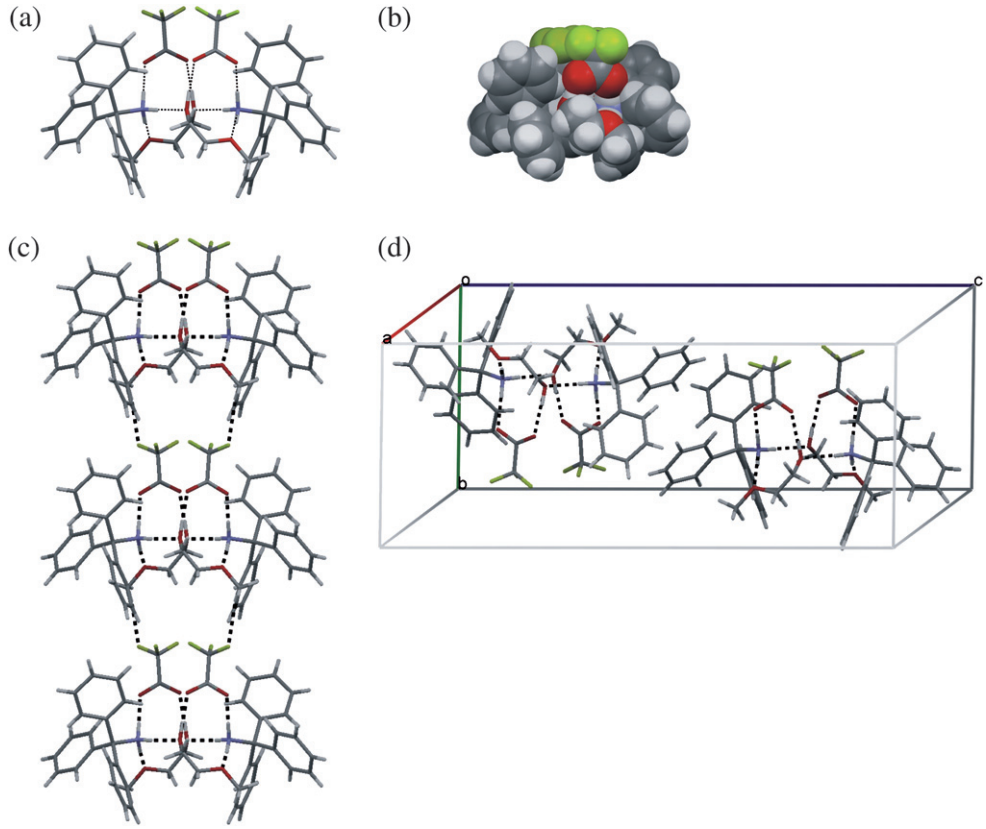

Fig. 8 Packing diagram for **X**: (a) network of hydrogen bonds shown by dashed lines within the six-membered cluster, (b) space-filling representation of the cluster, (c) column of clusters sustained by CH···F interactions, (d) the SPE between adjacent clusters.

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